

POLYMER CATALYST SYSTEM

DuPont eyes new polyolefins business

A new "advance in polyolefins technology could be the start of a whole new business" for DuPont, according to the firm's new president and chief executive officer, John A. Krol. A breakthrough has been made that will allow DuPont to offer new polyolefins at very competitive prices, Krol suggested at a press conference in New York City.

Joseph A. Miller, senior vice president for R&D, went even further. "DuPont is now able to offer olefin polymers never available before," he said, adding that the new technology could generate a multi-million-dollar business for the firm.

The advance resulted from cooperation between DuPont and Maurice S. Brookhart, professor of chemistry at the University of North Carolina, Chapel Hill. The keys to the new polyolefin technology, C&EN has learned, are catalysts that Brookhart developed with his associates Lynda K. Johnson and Christopher M. Killian [*J. Am. Chem. Soc.*, 117, 6414 (1995)]. The new catalysts are palladium- and nickel-based complexes that convert ethylene and α -olefins to high molar mass polymers with unique microstructures.

The new catalysts, Brookhart tells C&EN, are the first reported for which simple variation of pressure, temperature, and ligand substituents allows access to ethylene homopolymers with structures that vary from highly branched, completely amorphous materials to linear, semicrystalline, high-density materials.

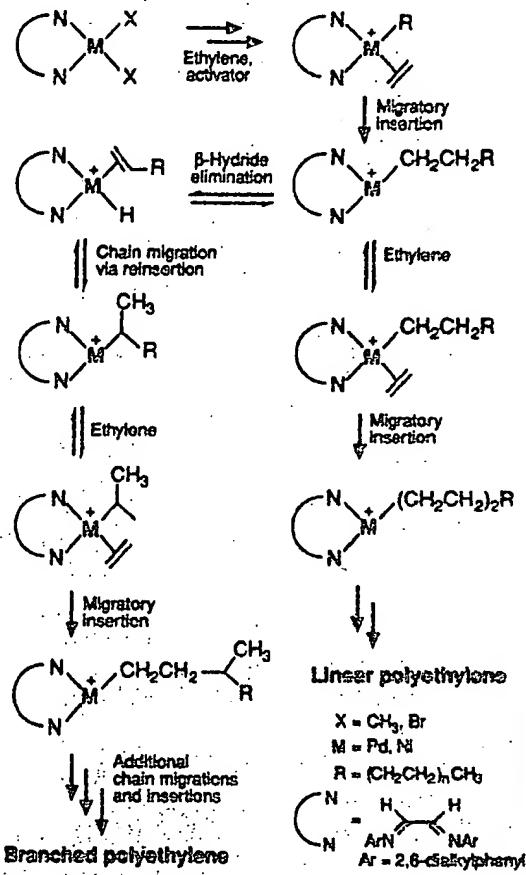
The Pd(II) and Ni(II) initiators are cationic metal complexes that incorporate bulky diimine ligands. Once activated, exposure of the palladium catalysts to ethylene, propylene, or 1-hexene produces high molecular weight polymers that are isolated as amorphous materials. Analysis of the polyolefins reveals extensive chain branching along the backbone of the molecule, with the branches randomly distributed and of variable length.

Brookhart says the amorphous polyethylene produced by these catalysts constitutes a new class of polyethylene that is far more highly branched than low-density polyethylene.

The activated nickel catalysts also trigger polymerization of ethylene and α -olefins and are easier to generate than the palladium catalysts. Polyethylene produced with these catalysts may be either highly branched or only moderately branched, with methyl branches predominating. The extent of branching is a function of temperature, ethylene pressure, and catalyst structure. Branching increases as the temperature rises. At higher ethylene pressures, less branching occurs, although polymer yields and molecular weights are similar.

Mechanistic studies show that the state the catalyst exists in most of the time (resting state) in polymerization of ethylene is an alkyl ethylene complex. Following migratory insertion of this species, a new metal alkyl cation is formed that may be trapped immediately by ethylene—leading, after insertion, to a linear chain segment. Or the metal alkyl cation may undergo chain migration before trapping by ethylene, resulting in chain branching. The extent of chain migration—and thus the extent of branching—can be controlled

Polymerization can yield both branched and linear polyethylenes



by physical process parameters. Because of the steric hindrance from the bulky diimine ligands, chain propagation rates are greater than chain transfer rates, leading to high molecular weights.

Brookhart says the nickel catalysts have very high activities, comparable with those of metallocene catalysts used in some commercial polyolefin processes. Turnover frequencies at room temperature are about 2×10^5 per hour in very dilute solutions.

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Meanwhile, in a related development, Brookhart's lab has produced the first examples of metal-catalyzed copolymerization of nonpolar monomers—ethylene or propylene—with polar alkyl acrylates to give high molecular weight copolymers [*J. Am. Chem. Soc.*, 118, 267 (1996)]. Similar to the corresponding ethylene homopolymers, the ethylene copolymers are amorphous, highly branched materials. The ester groups are located predominantly at the ends of the branches, and the rates of polymerization are considerably less than those for homopolymerization of ethylene.

Brookhart says these are the first transition-metal catalysts capable of polymerizing ethylene and propylene with functionalized vinyl monomers to high molecular weight polymers by a coordination-type polymerization.

DuPont has filed a patent application on the technology with about 500 claims. Miller said the patent deliberately was made as broad as possible, covering composition of matter, processing, and products. If all goes well, he believes it will take about five years to commercialize the technology.

Joseph Haggin

Federal shutdown threat put off to March 15

Major parts of the federal government are still up and running thanks to an agreement between Congress and President Clinton on a continuing resolution, effective through March 15. Most affected agencies—including the Environmental Protection Agency, the National Science Foundation, and the National Institute of Standards & Technology—are being funded at the level set by House-Senate conference reports on their fiscal 1996 appropriations bills. Those bills were vetoed by Clinton.

But to entice Clinton to sign this third continuing resolution, Congress agreed to fund at 75% of their fiscal 1995 spending levels a number of programs the majority wanted terminated. Congress also backed off from some provisions that would have restricted the actions of several agencies.

For example, under its fiscal 1996 appropriations bill, EPA would have been prohibited from proposing a drinking water standard for radon and from implementing and enforcing wetland pro-

All agencies are cut back in latest continuing resolution

\$ millions	1995 ^a funding	1996		
		Administration request	Continuing resolution	% change 1995-96
NASA	\$14,377	\$14,260	\$13,821	-4%
Science, aeronautics & technology	5,515	5,510	5,846	+6%
EPA	6,841	7,359	5,769	-13%
Environmental programs & management	2,150	2,647	1,550	-28%
Science & technology	539	546	525	-3%
NSF	3,360	3,359	3,179	-5%
Research & related activities	2,245	2,454	2,274	1%
Education & human resources	606	599	599	-1%
Commerce science & technology	2,953	3,611	2,707	-8%
Oceanic & atmospheric research	240	271	226	-6%
NIST	700	1,023	655	-6%
Advanced Technology Program	341	491	258	-25%
Department of Energy	857	1,016	741	-14%
Fossil R&D	424	436	376	-11%
Conservation R&D	433	580	365	-16%
OSHA	312	346	254	-15%
TOTAL	\$28,500	\$29,951	\$26,481	-7%

^a Includes rescissions signed into law July 27, 1995.

Source: P.L. 104-99, conference reports on fiscal 1996 appropriations bills

tection programs. EPA can now do so, at least until March 15.

But Congress cut EPA's budget severely for 1996—down 13% to \$5.8 billion. Funding for environmental programs and management is down 28% to \$1.6 billion. Given that budget, EPA says it will have to furlough people—for example, have them work one day without pay each two-week pay period—or perhaps even fire them.

One program saved by the latest continuing resolution is the NIST Advanced Technology Program. Congress targeted ATP for elimination—the Republicans consider it a prime example of "corporate welfare." ATP will receive 75% of its fiscal 1995 funding until March 15. That would be \$256 million on an annual basis, according to NIST spokesman Michael Newman. Although this will allow funding of existing grants, Newman says no new competitions for projects will be undertaken.

Other parts of NIST receive full funding under the continuing resolution. On an annual basis, that means \$259 million for laboratory operations, \$80 million for the Manufacturing Extension Program, and \$60 million for construction and renovation of NIST labs.

NSF also is funded at a rate governed by its fiscal 1996 conference report. Its research and related activities account actually increased slightly in fiscal 1996. But although NSF seems to be recovering rapidly from the two shutdowns, the uncertainty is taking a toll.

NSF's chemistry division conducts

most of its peer review by mail, and, despite a huge backlog of incoming mail, that process was only somewhat hindered by the shutdown, says division director Janet G. Osteryoung. Material could not be put in the mail to panelists. But, she points out, the division is required to make all its award recommendations by the end of June, so its fiscal year is effectively half over. Without a firm budget, there is more and more difficulty in making decisions. NSF has told all awardees to expect delays in getting their money.

University researchers who rely heavily or entirely on NSF support are beginning to feel the pinch. Robert Wild, professor of chemistry at Purdue University, West Lafayette, Ind., says: "People who are expecting decisions are delayed. Others are having difficulty in getting authorization to start spending on the grants."

Richard N. Zare, professor of chemistry at Stanford University and a member of the National Science Board, NSF's governing body, believes the damage caused by the shutdowns has already occurred, and in many cases the damage will last a long time. "Somewhere there is going to be lost funding, and somewhere somebody has to pay for it. The government is not going to continue to backdate things. It can't legally," he says. The bigger losses are harder to calculate. "The loss in morale is difficult to quantify, but it's real. What about the loss of opportunity? We cannot measure this loss."

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